

IMPROVEMENTS APPLIED TO METHODS
OF PREPARING INORGANIC AEROGELS

French Patent No. 130,417
Petitioned on 30 November 1967 at 1548 hours in Paris
Delivered by Decree of 20 April 1969
(Official Patent Bulletin, No. 22 of 30 May 1969)

Inventors: J. T. Stanislas, J. Teichner,
A. N. Gilbert and A. Nicolaon

Translation of "Perfectionnements Approtes Aux Procèdes
De Aerogels Mineaux", 7 pages.

(NASA-TT-F-14791) IMPROVEMENTS APPLIED TO
METHODS OF PREPARING INORGANIC AEROGELS
(Techtran Corp.) 13 p HC \$4.00 CSCL 07B

N74-21775

Unclas
G3/06 37274



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546
DECEMBER 1973

IMPROVEMENTS APPLIED TO METHODS
OF PREPARING INORGANIC AEROGELS

French Patent No. 130,417

Ministry for Industry

No. 1,568,817

Patent Office

International Classification: C 01 b

Inventors: J. T. Stanislas, J. Teichner,
A. N. Gilbert and A. Nicolaon

National Center for Scientific Research
Domiciled in France. (Paris)

Petitioned on 30 November 1967 at 1548 hours in Paris
Delivered by Decree of 21 April 1969
(Official Patent Bulletin, No. 22 of 30 May 1969)

(Patent whose delivery was postponed in execution of Article 11,
Sec. 7, of the law of 5 July 1844, as modified by the law of
7 April 1902)

The invention concerns methods for preparation of inorganic aerogels,
especially of the silica variety, i.e., gels in which the dispersion medium
is a gas or a vapor. /1*

It has as its main goal the performance of the above-mentioned methods
such that they satisfy, in a unique and exemplary manner, the various require-
ments of presentday practice insofar as concern speed of production, cost,
quality and special properties (opening new possibilities of use) of products
which these methods make possible.

It consists, chiefly, in the methods of the kind involved, in dissolving
in a non-aqueous solvent a hydrolyzable silicon compound, preferentially
volatile, releasing volatile products by hydrolysis; in adding to this solu-
tion a quantity of water sufficient to hydrolyze the aforesaid compound and,

*Numbers in the margin indicate pagination in the foreign text.

finally, in subjecting the whole to conditions of temperature and pressure such that the critical point of aforesaid solvent is reached or even surpassed..

It consists, aside from this main provision, in certain other provisions which are preferentially used together at the same time and which will be especially discussed in the following.

It aims more particularly for certain methods of application as well as for certain methods of carrying out the aforesaid provisions. It aims even more particularly, and here in the field of new industrial products, towards aerogels produced by developing methods of the type in question involving application of the aforesaid provisions.

The invention will be well understood, in any case, by using the descriptive material following below as well as the appended figure complementing the latter and submitted, of course, for guidance purposes.

The one figure shows, in diagrammatic cross-section, an installation suitable for operation of the method according to the invention.

According to the invention, and, more especially, according to those of the methods of application, as well as according to those of the methods of production of its various parts, to which it appears there may be occasion for granting preference, it being proposed to prepare silica aerogels, the following describes how it is to be done.

It is already understood how to manufacture silica aerogels by precipitating the gel by acidifying a solution of sodium silicate. This gel is washed with distilled water up to point of total removal of the acid and salts coming from the neutralization. The water is replaced as totally as possible by an organic solvent and then the gel-impregnated solvent is dried under hyper-critical conditions in the autoclave.

Now, the gel washing operation carried out to remove the salts and the operation for replacing the water by the solvent are extremely time-consuming and, owing to this, quite expensive in personnel costs.

Thus, in order to be more specific, it is pointed out that it is necessary to subject the gel just precipitated by acidifying the silicate solution to

about fifty washings in order to totally remove the salts and traces of acid.

In order to cope with these disadvantages, consistent with the invention, /2
a hydrolyzable silicon compound is dissolved in a non-aqueous solvent, preferentially volatile, releasing volatile products by hydrolysis. Added to this solution is a quantity of water sufficient to hydrolyze the aforesaid compound. Finally, the whole system is subjected to conditions of temperature and pressure such that the critical point of the aforesaid solvent is reached, or even exceeded.

In practice, it is advantageous to select methyl orthosilicate $\text{Si}(\text{OCH}_3)_4$ in its capacity of a hydrolyzable compound of silicon. The organic solvent generally used is methanol. It is, nevertheless, possible to likewise use silicon tetrachloride although there then occur problems involving resistance of the materials to the corrosive action of HCl which is released.

The quantity of methyl orthosilicate used, taking into account the quantity of methanol, is selected greater than 5% and, preferentially, less than 30% by volume. In general, it is on the order of 10%, a proportion with which the best values have been obtained. (It is pointed out that this quantity is a function of the pH conditions.)

Insofar as concerns the quantity of water used to hydrolyze the silicon compound, it is preferentially taken between 1 and about 5 times the stoichiometric quantity when the medium is acid (addition of acetic acid) or neutral. In the case of a basic medium (addition of NH_3), gelation occurs starting from ordinary temperature when the quantity of water exceeds 2 times the stoichiometric quantity. This premature gelation, furthermore, presents no disadvantage.

In order to produce conditions of temperature and pressure allowing the critical point of the solvent to be reached, it is advantageous to place the solution of the hydrolyzable silicon compound inside an autoclave in which there is likewise placed, preferentially without any mixture taking place with the solution of the silicon compound, a supplementary quantity of the solvent sufficient for the critical point of the solvent to be reached taking into account the volume of the autoclave.

The autoclave is closed as soon as the solvent and the solution of the silicon compound are introduced. The temperature is then raised as linearly as possible to a value greater than the critical temperature of the solvent after which the solvent vapor is removed. Once the pressure has returned to normal, the autoclave is purged using an inert dry gas to remove all condensable vapors. The temperature is then returned to normal after closing the autoclave valves in order to avoid any condensation of atmospheric water vapor.

In order to carry out this method, it is advantageous to use the apparatus depicted in the single figure and which includes an autoclave 1 which can be closed by a lid 2 and connected by pipes 3 and 4 respectively to an inert gas tank 5 (with interposition of drying columns 6) and to a tank 7 intended to receive the solvent after condensation in a refrigerant 8. Valves 9 and 10 are installed respectively in pipes 3 and 4. A thermal probe 11 and a manometer 12 allow the variations of temperature and pressure to be followed inside autoclave 1.

In order to illustrate what has just been said, a numerical example of implementation of the method according to the invention will be described with utilization of the apparatus of Figure 1.

500 ml of methyl orthosilicate is dissolved in 4,500 ml of methanol. The solution obtained has about 10% of methyl orthosilicate. This solution is then brought to 0°C and a quantity of water corresponding to 2 to 5 times the stoichiometrical quantity of reaction 1 is added:



This solution is poured into a jar which is placed in autoclave 1 which has an inside volume of 300 liters. Alongside of the tube containing the solution, another jar containing 95 liters of methanol is placed. This is a quantity sufficient for the critical pressure to be exceeded when the temperature exceeds the critical point.

With the autoclave closed, the temperature is brought to 260°C (18°C above the critical temperature) in 2 h 30 min. The temperature rise takes place at the rate of 1.6°C/min. At the end of heating, the methanol vapor is removed by opening valve 10. The vapors are recovered in tank 7.

Once the pressure has returned to atmospheric pressure (removal of the methanol vapor requires about 30 min), valve 9 is opened and, leaving valve 10 likewise open, the autoclave is purged by means of about 3 m³ of nitrogen. Valves 9 and 10 are then closed and the autoclave is cooled down to ambient temperature.

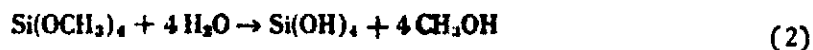
The autoclave can then be opened and about 200 g of aerogel occupying a volume of about 5 liters may be taken out.

Total time elapsed for the preparation is about 4 hours.

The aerogels produced in this way are characterized by their porosity. This porosity can be investigated, for example, by low-temperature adsorption of gases and using the mercury porosimeter.

It has been generally demonstrated that the adsorption of argon at -195°C allows determination of the volume of the micropores (radius of pores < 100 Ångstroms). The porous volume determined by penetration of mercury is the volume of the macropores (radius of the pores > 290 Ångstroms).

The precipitation reaction of the silica is totally described by equation 1/3 1 shown above. Indeed, it is a more or less polycondensed polysilicic acid which precipitates. Under these conditions, the aerogel produced does not satisfy the formula SiO₂ but rather the formula SiO₂, nH₂O in which n < 2. We have n = 2 in the case where the reaction would be limited to the formation of the monomeric silicic acid Si(OH)₄ according to equation 2:



As the polycondensation of this acid, leading to the SiO₂ silica gel, is performed with removal of water, the aerogels prepared under the stoichiometric conditions corresponding to reaction 2 lose a little water during the autoclave processing.

It became clear that in an acid medium (0.175 N with acetic acid) the precipitation is very incomplete when the quantity of water used is kept strictly stoichiometric (equation 1). The aerogel produced under these conditions by hydrolysis of a solution with 10% methyl orthosilicate in methanol

(E₁ gel) has a very low porosity with respect to those produced with an excess of water. As soon as a quantity of water doubles that of the stoichiometry of reaction 1 is used, the aerogel produced (E₂) occupies the complete total of the volume of the alcoholic solution of methyl orthosilicate initially placed in the autoclave and has considerably improved textural characteristics. Gels prepared in this way have had a total porosity in the vicinity of 18 cm³/g (E₃ gel). When the concentration of water becomes too great (E₄ gel), the porosity decreases markedly.

The results compiled in Table I below show that all of the textural properties of aerogels produced by this method pass through a maximum for a quantity of water included between 2 and 5 times the stoichiometric quantity of reaction 1:

TABLE I. PRECIPITATION IN ACID MEDIUM

Aerogel	$\frac{H_2O}{Si(OC_2H_5)_4}$	S (m ² /g)	V _{PA} (cm ³ /g)	V _{PN} (cm ³ /g)	V _P (cm ³ /g)
E ₁	2	390	0,15	0,18	2,7
E ₂	4	865	0,72	1,82	11,6
E ₃	10	688	0,62	1,72	17,3
E ₄	20	405	0,40	1,52	7,2

Note: Commas indicate decimal points.

In which:

S = specific surface measured with nitrogen by the Brunauer-Emmett-Teller (BET) method;

V_{PA} = porous volume measured with argon;

V_{PN} = porous volume measured with nitrogen;

V_P = porous volume determined by mercury penetration.

From the findings summarized in Table II (below), it becomes clear that a similar gradual development is observed in a neutral medium. The porosity accessible to gases in the absorbed state (V_{PA} and V_{PN}) vary as a function of

the quantity of water introduced in the same way as in an acid medium. On the other hand, the volume of the large pores (V_p) is not affected by a great excess of water (Table II).

TABLE II. PRECIPITATION IN NEUTRAL MEDIUM

Aerogel	$\frac{H_2O}{Si(OCH_3)_4}$	S (m ² /g)	V_{pa} (cm ³ /g)	V_{pn} (cm ³ /g)	V_p (cm ³ /g)
E ₁	2	306	0,23	0,40	7,9
E ₂	4	700	0,71	1,53	10,7
E ₃	10	590	0,53	1,58	15,4
E ₄	20	523	0,54	1,48	16,3

Note: Commas indicate decimal points.

Finally, in a basic medium (0.5 N in ammonia), the precipitation is much more complete than in an acid or neutral medium even with only the stoichiometric quantity of water as is shown by the weights of gel produced.

/4

Under these conditions, the first silica sol is much less stable and, as soon as the concentration of water is greater than double the stoichiometry of reaction 1, there is a partial precipitation of the silica starting with the introduction of the methyl orthosilicate into the hydrated methanol. For this reason, the investigation of the effect of concentration of water in alkaline medium cannot be done for values of the $H_2O/Si(OCH_3)_4$ ratio greater than 4. Nevertheless, the preparation of aerogels remains possible by introducing into the autoclave not a homogeneous liquid solution but a heterogeneous solution already in part gelated or precipitated.

TABLE III. PRECIPITATION IN ALKALINE MEDIUM

Aerogel	$\frac{H_2O}{Si(OCH_3)_4}$	S (m ² /g)	V_{pa} (cm ³ /g)	V_{pn} (cm ³ /g)	V_p (cm ³ /g)
E ₁	2	820	0,61	1,64	4,6
E ₂	4	697	0,51	2,06	5,3

Note: Commas indicate decimal points.

It appears from the results of Table III that the aerogels produced in an alkaline medium have a macroporosity (V_p) much less developed than that of aerogels precipitated in an acid or neutral medium although their microporosities (V_{pN} , V_{pA}) are comparable. They have a very special appearance. Whereas the aerogels prepared by this method in an acid or neutral medium are white and opaque, those produced in an alkaline medium are colorless and perfectly transparent, even when about 1 cm thick.

Finally, the effect of methyl orthosilicate concentration in a slightly acid medium (0.175 N in acetic acid) was studied in the presence of a quantity of water corresponding to the stoichiometry of reaction 2.

TABLE IV.

Aerogel	[Si (OCH ₃) ₂] Percentage in volume	S (m ² /g)	V_{pA} (cm ³ /g)	V_{pN} (cm ³ /g)	V_p (cm ³ /g)	d_a (g/cm ³)
E ₁₁	5	524	0,23	0,21	1,2	0,27
E ₂	10	865	0,72	1,82	11,6	0,04
E ₁₂	20	805	0,68	1,55	10,0	0,10
E ₁₃	30	774	0,60	1,46	4,0	0,16
d_a = Apparent density of the solid						

Note: Commas indicate decimal points.

It becomes clear from the values compiled in Table III that the aerogel prepared beginning from a solution with 5% by volume of methyl orthosilicate in methanol has a microporosity to a greater extent than that of the other solids. This observation may be explained by the fact that, for a concentration of methyl orthosilicate less than 10%, the solid taken out of the autoclave occupies a volume quite less than that of the initial solution. However, as soon as the concentration is equal to 10%, the dry gel occupies a volume quite close to that of the initial solution, and its apparent density is consequently appreciably proportional to the concentration in methyl orthosilicate as is made clear by the experimental values (cf. last column of Table IV).

It is then normal for the porous volumes measured by adsorption of gas or by porosimetry with mercury to decrease when the concentration of methyl

orthosilicate goes from 10 to 30%. On the other hand, the specific surface is only barely affected by this factor (Table IV).

The thermal stability of aerogels prepared consistent with the invention has likewise been studied. For this, an aerogel precipitated by hydrolysis of a solution with 10% methyl orthosilicate in a 0.175 N acetic acid medium in the presence of a quantity of water corresponding to the stoichiometry of reaction 2 was subjected to a thermal treatment for 8 hours in air at temperatures ranging between 300 and 900°C. /5

It was found that heating to 500°C considerably improved the macroporosity of the aerogels measured with mercury (16.5 cm³/g instead of 11.1). The porous volume accessible with mercury is not clearly less than that of the initial solid except in the case of processing temperatures greater than 700°C. On the other hand, the porosity accessible to gases in the absorbed state (V_{pN} and V_{pA}) decreases uniformly when the temperature increases. The results obtained are summarized in Table V which follows.

TABLE V. INFLUENCE OF THERMAL PROCESSING OF AN EIGHT HOUR DURATION ON THE TEXTURE OF A SILICA GEL PREPARED STARTING FROM METHYL ORTHOSILICATE

Processing temperature (°C)	S (m ² /g)	V_{pA} (cm ³ /g)	V_{pN} (cm ³ /g)	V_p (cm ³ /g)
Initial aerogel	860	0,71	1,81	11,1
300	1 004	0,70	1,48	13,1
500	800	0,56	1,26	16,5
700	477	0,37	0,90	10,5
900	162	0,14	0,30	6,5

Note: Commas indicate decimal points.

It results from this investigation that the macropores of silica aerogels prepared beginning from methyl orthosilicate have a good thermal stability up to 700°C.

The porous volume measured by mercury penetration of aerogels heated to this temperature is not decreased on a practical basis with respect to that of the initial aerogel in spite of the very clear decrease in the porosity

accessible to the gases in the absorbed state (V_{pN} , V_{pA} and S). The apparent density as well as the appearance of the aerogels are not appreciably modified as long as the heating temperature does not exceed 700°C. Such solids would appear to be especially well-suited as thermal insulators which could be used in a very wide temperature range (-200°C to +700°C).

The autoclave presentation in the presence of methanol has the effect of causing the aerogels to become more or less hydrophobic for the hydroxyl groups of the silica are more less esterified by the methyl alcohol. They only adsorb a moderate quantity of water vapor and when the esterification rate of the OH is great, after a prolonged heating under pressure in the autoclave, they are not wetted by the liquid water.

The aerogels have the property of gelling the organic liquids or the aqueous solutions when they are added in a very small quantity (5% by weight) to the latter. They can also be used to increase the viscosity of such liquids.

Consequently, there is thus available a multipurpose method for preparing silica aerogels whose characteristics are sufficiently clear from the above that it is useless to further emphasize the subject and which have, with respect to those already in existence, numerous advantages, chiefly that of avoiding the gel washing operation as well as that of replacing the water impregnating the gel by a solvent.

As is understood, and as has been made clear from the above, the invention is in no way confined to those of its modes of application, nor to those of the modes of production of its various parts, having been especially indicated. It encompasses, on the contrary, all of the variations, chiefly those according to which the present method is applied to alcoholates or chlorides of elements other than silicon.

Summary

The invention has the goal of improving the methods for preparation of inorganic aerogels, especially silica aerogel, whose improvements have the following characteristics of which the first one, in particular, can be taken either separately or according to certain combinations with others:

1. a non-aqueous solvent is used to dissolve a compound of hydrolyzable silicon, preferentially volatile, producing volatile products by hydrolysis. There is added to this solution a quantity of water sufficient to hydrolyze the aforesaid compound and, finally, the whole system is subjected to conditions of temperature and pressure such that the critical point of the aforesaid solvent is reached and even exceeded;

2. the aforesaid hydrolyzable compound is made up by methyl orthosilicate and the aforesaid solvent is made up by methanol;

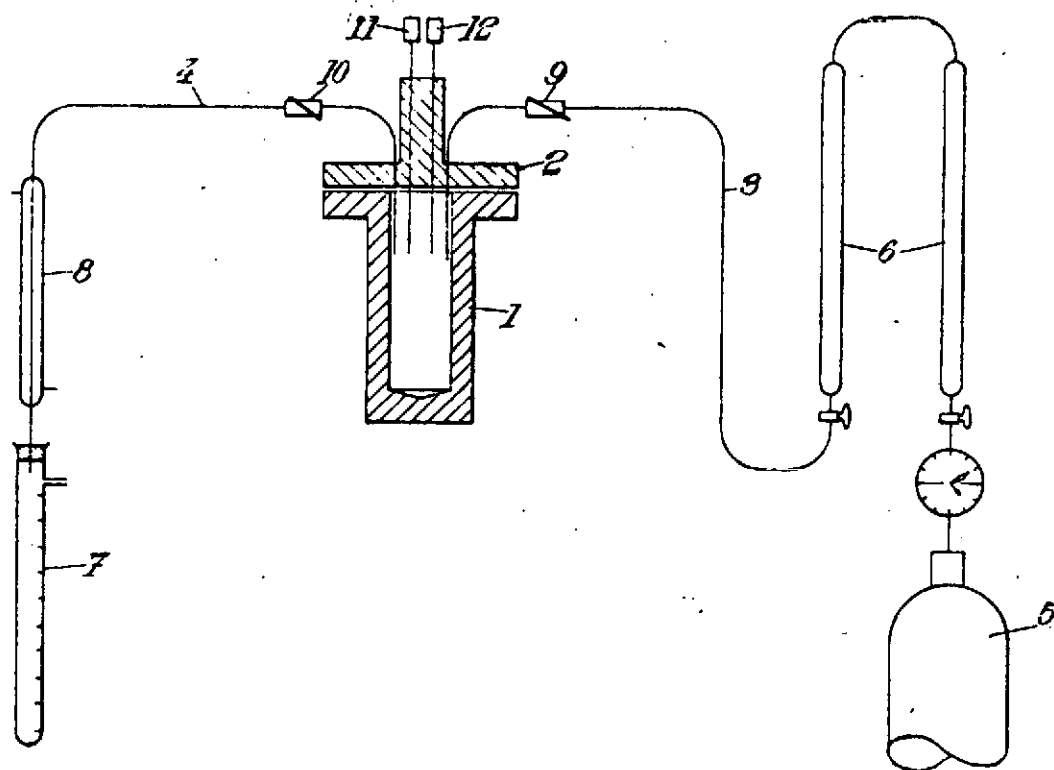
3. the quantity of methyl orthosilicate dissolved in methanol is on the order of 10%;

4. the quantity of water utilized to hydrolyze the silicon compound is selected preferentially between 1 times and about 5 times the stoichiometric quantity when the medium is acid or neutral.

National Center for Scientific Research

Power of Attorney: L. Demon

NATIONAL CENTER FOR SCIENTIFIC RESEARCH



Translated for the National Aeronautics and Space Administration under contract No. NASw-2485 by Techtran Corporation, P.O. Box 729, Glen Burnie, Maryland 21061. Translator: Rowland A. Wells.